

RESEARCH PAPER

Synthesis of Serrated GaN Nanowires for Hydrogen Gas Sensors Applications by Plasma-Assisted Vapor Phase Deposition Method

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ABSTRACT

Nowadays, the semiconductor nanowires (NWs) typically used in hydrogen gas sensors. Gallium nitride (GaN) with a wide band gap of 3.4 eV, is one of the best semiconductors for this function. NWs surface roughness have important role in gas sensors performance. In this research, GaN NWs have been synthesized on Si substrate by plasma-assisted vapor phase deposition at different deposition time, without using any catalyst. The precursors were gallium (Ga) metal and nitrogen (N) plasma. The GaN NWs were characterized by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), photoluminescence (PL) and Raman Spectroscopy. The results indicate the serrated morphology for hexagonal structure of GaN NWs. The band gap energy of GaN NWs was obtained about 3.41 eV. The Raman results show two Raman active optical phonons at 563 cm^{-1} and 720 cm^{-1} due to $E_2(\text{high})$ and $A_1(\text{LO})$, respectively and indicates a good crystallinity of the NWs with the presence of defects in the crystal lattice.

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INTRODUCTION

Hydrogen is one of the promising candidates to replace fossil fuels and overcome the problems of air pollution and global warming. Hydrogen gas is odorless, colorless and highly flammable and therefore, safety will be a vital and challenging subject during storage, delivery, and H_2 usage. In order to avoid the risk of hydrogen leakage, hydrogen gas sensor should be used for fuel cell leak detection in autos and industrial process emissions, seriously [1–3]. Developing accurate sensors for different conditions has become very important. Also, most of the gas sensors are based on semiconductor NWs and created by formation of metal-semiconductors NWs-metal contact. GaN nanostructure are used for hydrogen

gas sensing because of the sensitivity to surface charge [4–6]. In addition, GaN nanostructure and sensors based on GaN can be operated at higher temperatures than conventional semiconductors and conventional Si-based devices [7].

Most recently, materials such as GaN, ZnO, SnO_2 , TiO_2 and carbon nanotubes have been investigated for hydrogen gas sensing applications. Also one dimensional (1D) nanostructured materials such as NWs, nanorods and nanotubes are used as basic building blocks for hydrogen gas sensors. It has been reported that the properties and device performances of 1D nanostructured materials are strongly dependent on surface morphology [2,6,8,9]. Several reports have been published for better hydrogen gas sensor performance of GaN

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NWs with rough surface than GaN microstructures which is most probably attributed to higher specific surface area [6,10].

In this work, serrated NWs of GaN were synthesized by plasma-assisted vapor phase deposition technique. GaN were deposited on Si substrates at constant temperature (800°C) and various deposition times.

MATERIALS AND METHODS

GaN NWs were produced by using deposition equipment from Plasmafanavar Amin Co, Iran [11–13]. Si wafer was used as substrate without any catalyst and washed using Radio Corporation of America method, and dried at room temperature (RT). For our experiment, a 800-nm-thick nonconductor Si_xN_y layer was grown on silicon (100) substrates by plasma nitriding. Deposition equipments had a horizontal quartz tube with 4 inches of diameter in a tube furnace and there were two parallel stainless steel electrodes with 3cm distance. Si substrates were placed on top of an alumina boat contained of Ga metal. High purity Ga metallic, N₂ and Ar high purity of 99.999% was used as the source material. GaN NWs were grown under 2 Torr pressure of reaction chamber, volume of gases were controlled by using accurate mass flow controller. N₂ and Ar were introduced to the furnace with 200 and 100 sccm, respectively. Temperature of furnace was increased at a rate of 30°C/min and then maintained at 800°C for 240min. A 550V, 2A (current) at 10 kHz was applied to electrodes. N₂ and Ar plasmas were generated between the

electrodes and produced active N₂ and Ar radicals and ions for creation of GaN NWs, after the reaction furnace was cooled down to RT. The morphology of GaN NWs was analyzed by field emission scanning electron microscopy (FESEM). The structural characterizations were carried out using energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) using cobalt radiation with λ=1.79 Å. The optical properties of the GaN NWs were investigated using photoluminescence spectrum (Cary Eclipse Fluorescence Spectrophotometer) at RT. The Raman spectroscopy (Bruker Dispersive Raman Spectrometer) measured at RT with 785nm multiple laser, as excitation source.

RESULTS AND DISCUSSION

Fig. 1. shows the X-ray diffraction pattern of the GaN nanostructures. The Three peaks (1 0 0), (1 0 1), and (1 1 0) of GaN nanostructures are located at 37.96, 43.08, and 68.76, respectively, demonstrating that The GaN NWs have been grown in hexagonal wurtzite structure with lattice constants of a=3.18 Å and c=5.18 Å, consistent with the reported values of bulk GaN[14]. The intensity of the peak depends on the number of NWs grown along the lattice orientation in the nanostructure films. The strongest (1 1 0) peak with increasing deposition time, indicates that the maximum NWs grow along [1 1 0] orientation. Broadening of XRD peaks could be attributed to grain refinement and internal strain of sample.

Fig. 2. shows FESEM images of the synthesized samples at different deposition time. The light-

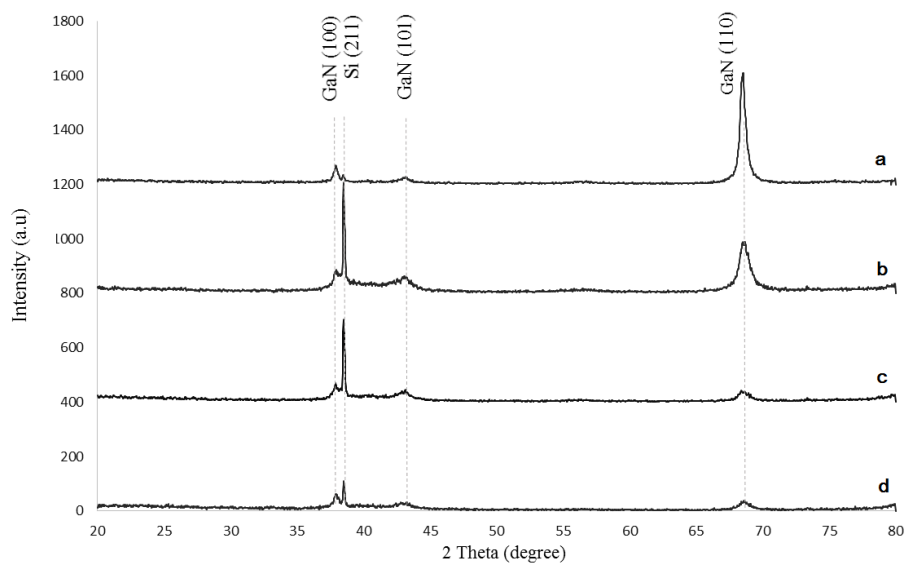


Fig. 1. X-ray diffraction pattern of GaN nanostructures at different deposition time; (a) 4h, (b) 3h, (c) 2h and (d) 1h.

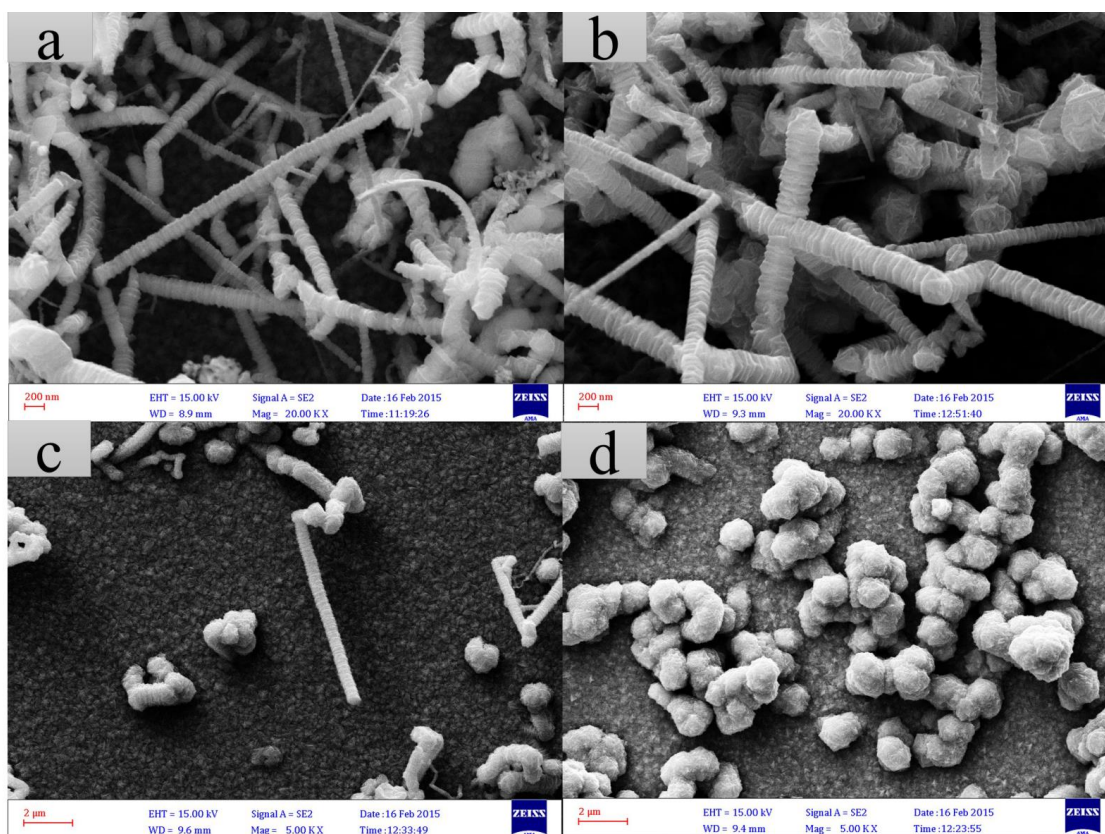


Fig. 2. FESEM images of the synthesized GaN NWs at different deposition time; (a) 4h, (b) 3h, (c) 2h and (d) 1h.

yellow layer is composed of NWs, and the NWs can be observed clearly with about 50-200 nm in diameter and 3-5 μm in length. Fig. 2(c,d) shows cauliflower GaN structure and GaN NWs growth from it. Fig. 2(a) and 2(b) shows the existence of serrated morphology for grown NWs and high surfaces roughness with maximum surface-to-volume ratio. So, a lot of surface atoms on the NWs are ready to react with the target gas, which is advantageous for the applications of the NWs in the gas sensor applications [6,10].

At low magnification in Fig. 3, it can be noticeably observed that the sample is composed of a huge number of NWs. It's considerable to note that the morphology of the formed NWs seems to be serrated with rough surface, and cross each other also dispersed randomly over a large area of the substrate.

Fig. 4. clearly shows prominent phonon modes at ~ 563 and 720 cm^{-1} in the Raman spectra of the samples grown at various deposition time. The peaks at 563 and 720 cm^{-1} can be assigned to $E_2(\text{high})$ and $A_1(\text{LO})$ Raman modes corresponding

to wurtzite GaN, respectively [15]. Fig. 4(e) shows Si substrate Raman spectra and strong substrate peak is observed at 520 cm^{-1} denoted as $\text{Si}_{\text{Lo-To}}$ which corresponds to bulk Si longitudinal optical-transverse optical [16]. The peak detected around 660 cm^{-1} may be recognized with surface optical (SO) modes. According to previous reports [6,10,15,17], the disordered surface of serrated

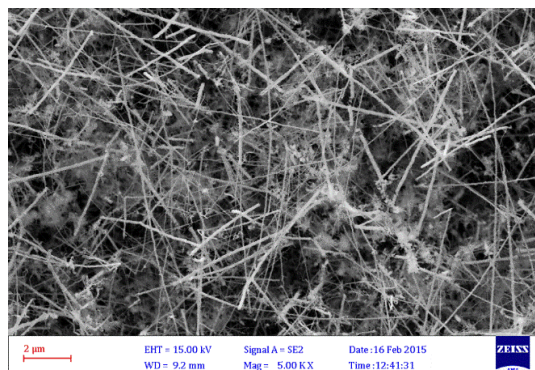


Fig. 3. FESEM image of the synthesized GaN NWs at 3hour with low magnification.

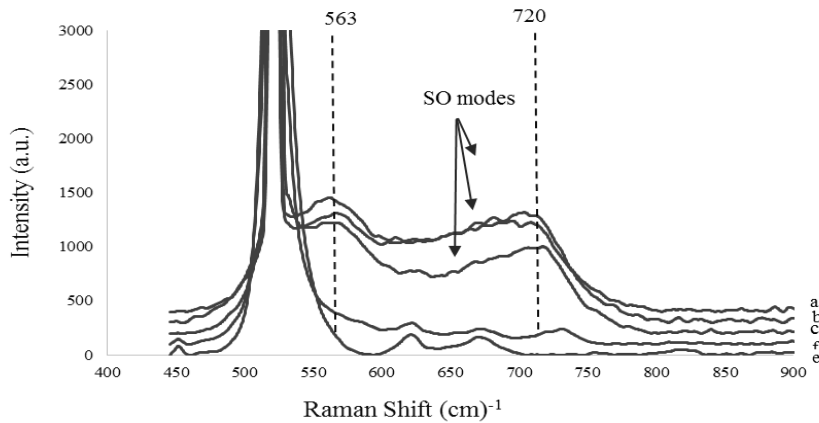


Fig. 4. Raman spectra of GaN nanostructures grown at different deposition time, measured at RT; (a) 4h, (b) 3h, (c) 2h, (d) 1h and (e) Si substrate.

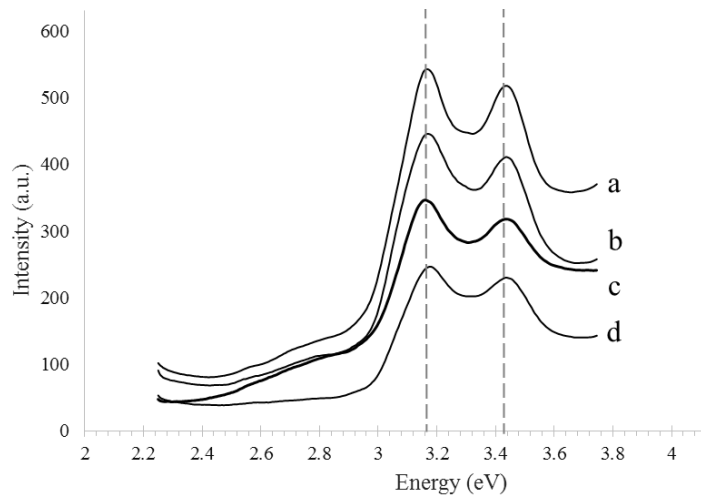


Fig. 5. Room temperature PL spectra for GaN nanostructures synthesized at various growth deposition time; (a) 4h, (b) 3h, (c) 2h and (d) 1h.

GaN NWs may be caused these surface optical modes.

Room temperature PL spectra of the samples at various deposition time show two peaks in the range of 3-3.6 eV using a 290 nm excitation. The emission peak at 3.44 eV is associated with the near-band-edge emission of GaN and that is an intrinsic process. The peak at 3.17 eV may be assigned to free-to-bound (FB) recombination related emission [18]. Ga clusters in the absence of N will energetically favour the creation of a deep level acceptor state, which may radiatively recombine with the free electron to give the FB band emission [19,20].

CONCLUSION

Serrated GaN NWs have been grown by plasma-

assisted vapor phase deposition Method using Ga metal and N plasma as precursors, without using any catalyst. The XRD and FESEM results show that the NWs are hexagonal wurtzite GaN possessing rough surface suitable for gas sensors applications. The results of Photoluminescence and Raman spectra showed the favorable optical properties of the grown NWs. These NWs possess good optical properties, which is obviously advantageous for the applications of the NWs in the nanodevices.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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